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Fe(III)-Mediated Electrooxidation of Pyridine and Several Derivatives to Produce a Novel n-Dopable Conducting Polymer

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Abstract

Pyridine and lutidine can be oxidatively electropolymerized in the presence of Fe(II) salts to give films of a new, n-dopable conducting polymer. Substoichiometric amounts of the Fe(II) salts are required to achieve efficient polymerization, implying that the metal is acting in a catalytic capacity. In its oxidized form, this new material exhibits strong absorbance at wavelengths shorter than ca. 400 nm. The material can be reversibly reduced over the range 0 to -0.8 V vs Ag/AgCl. Reduction leads to a decrease in the intensity of the short wavelength uv-vis band and appearance of a broad, long wavelength band in the 800-900 nm range, indicative of an n-doping process to produce a conductive material with low bandgap. These spectral changes are shown to be completely reversible. The potential dependence of the conductivity of the material is tested by examining the effectiveness of the film as an electrode material using a solution phase compound with two redox couples at potentials within and outside of the conducting region for the material. Both the oxidized and reduced forms of the polymer are insoluble in common organic solvents (e.g., methanol, acetone, chloroform, and DMSO).

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Introduction

To date, a great number of conducting polymer materials have been discovered and studied [1]. These materials can be synthesized in a variety of formats and compositions, giving materials with attractive mechanical, electrical and optical properties. Examples include poly(acetylene) [2-6] and poly(aniline) [7-14]. Our interest in such materials stems from their potential uses in thin film polymer batteries [15-18].

Doping of conducting polymers can occur either by p-doping (*i.e.* oxidation) or n-doping (*i.e.* reduction), which the ability to achieve either doping state dependent on the relative stability of the material toward oxidation or reduction. A few conducting polymers are known to be doped by both processes. For example, poly(acetylene) [2-6], poly(p-phenylene) [19-21] and poly(thiophene) [22-25] can all be both p- and n-doped. More common are materials that can only be p-doped. Examples include poly(aniline) [9-14, 26], poly(pyrrole) [27-33] and poly(phenylenevinylene) [34, 35]. For most materials that can be n-doped, this process only occurs at very negative potentials. There are few example of conducting polymers that only exhibit n-doping, especially at modestly negative potentials. However, recently, Yamamoto and coworkers have developed chemical routes to several n-dopable conducting polymers, such as poly(pyridine-2,5-diyl) [36-39], poly(quinolinediyl) [40] and its derivatives [41, 42]. These materials are made via a dehalogenation condensation that is catalyzed by an

organonickel reagent. A common structural motif in these materials is the presence of a π -deficient aromatic system with an electron withdrawing group, such as an imine nitrogen. It is significant that this electron withdrawing character makes oxidative routes to these materials problematic because the electron withdrawing groups make monomer oxidation unfavorable.

In this contribution, we report the production of a novel n-dopable conducting polymer by electrochemical oxidation of pyridine and several of its derivatives in the presence of Fe(II) salts, which appear to act catalytically in the reaction. Previous reports of pyridine oxidation describe production of a dimeric cation [43, 44] or pyridination [45, 46] of aromatics via chemical oxidation. To our knowledge, the present results represent the first example of pyridine oxidation to produce a conducting polymeric material. It is especially novel that, as will be described below, this material can be n-doped at relatively modest negative potentials.

Experimental Section

Materials. Acetonitrile (AN) was purchased from Aldrich Chemical Inc., purified by distillation in the usual manner, and stored over 3 Å molecular sieves. Pyridine and lutidine were purchased from Aldrich Chemical Inc. and were purified by distillation in the usual manner. N,N'-diphenyl-1,4-phenylenediamine (DPPD) was also purchased from Aldrich Chemical Inc. and was used after recrystallization from methanol.

Electrochemical Measurements. The cyclic voltammograms were obtained using a potentiostat (BAS model CV27) and are reported vs Ag/AgCl/NaCl(sat). Experiments were carried out in a three-electrode cell using a glassy carbon disk electrode (BAS, diameter: 3.0 mm) as the working electrode, a platinum wire (diameter: 0.2 mm, length: 60 cm coil) as the counter electrode and Ag/AgCl/NaCl(sat) as a reference electrode. Other conditions were: 25.0 ± 0.1 °C, scan rate = 50 mV/s, in the range from -0.8 V to 1.8 V using an acetonitrile solution containing 0.1 M LiClO₄, which was extensively deaerated using nitrogen gas.

Spectroscopy Methods. The uv-vis spectra were obtained using a diode array type uv-vis spectrometer (Hewlett-Packard HP8452). *In situ* uv-vis spectra were taken using an indium-tin oxide (ITO) electrode (0.9 mm x 50 mm) and quartz cell (optical length: 10 mm, width: 10 mm). Considerable care was taken to ensure the exclusion of both oxygen and water from the samples during the measurements.

Results and Discussion

Figure 1a shows a cyclic voltammogram (CV) of a 10 mM solution of lutidine in acetonitrile containing 0.1 M LiClO₄ as supporting electrolyte. Clearly, there is no redox activity for lutidine in this range (-0.8 - +1.8 V). Similar experiments with pyridine also show no redox activity over this range. Figure 1b shows the response for a solution of iron(II) perchlorate under the same conditions. The Fe(III)/Fe(II) redox couple is clearly observed from its quasi-reversible wave at +1.42 V. When both lutidine and iron (II) perchlorate are present in the supporting electrolyte, the solution immediately turns a green color, suggesting formation of a complex between the Fe(II) centers and lutidine. Figure 1c shows the result of repetitive cycling over the same potential range in this solution. It can be seen that the Fe(II) oxidation peak at ca. +1.5 is much larger and shifted to ca. +1.3 V, and the return (reduction)

peak is absent. This negative shift of the Fe(II) oxidation peak and the irreversibility of the oxidation suggest that an Fe(III) species catalytically oxidizes the lutidine under these conditions. With repetitive cycling, one observes the appearance and growth of a redox wave centered near -0.2 V. Figure 1d shows this wave more clearly and in expanded form in a solution that contains only 0.1 M LiClO₄ after 20 cycles under the conditions in Figure 1c. The fact that the response remains when the electrode is transferred to pure supporting electrolyte is clear evidence for deposition of a film on the ITO electrode surface. In fact, this film is visible on the electrode surface as a pale yellowish material. The wave in Figure 1d has the characteristic shape and appearance of an insulator-to-conductor transition (i.e. doping and undoping) for conducting polymers [1]. Very similar results are observed for the iron (II) perchlorate/pyridine system, with the caveat that the irreversible oxidation peak that is observed when both compounds are present is not shifted, appearing at ca. +1.5 V.

Figure 2 shows a CV for a film in pure supporting electrolyte that was prepared by potential cycling in a solution containing lutidine and Fe(II). In this case, the range is extended to more negative potentials. One can clearly observe a second, large redox response centered near -1.1 V, and a significant drop in current at potentials more negative than the peak potential. Note that the apparent "charging" current is large between ca. 0.0 and -1.8 V, and drops off both positive and negative of this range. We return to this point below. For both the lutidine and pyridine films in pure supporting electrolyte, a plot of scan rate (25 - 500 mV/s) versus the peak current for both the oxidation and reduction peaks near -0.2 V is linear, as expected for a surface-confined species [47]. The peak separation increases as a function of scan rate. This is not a consequence of solution phase resistance. Rather, it must be due either to sluggish charge transfer kinetics or intrinsic resistivity of the film. These films are thin, not degraded in air, and very resistant to a variety of common solvents. For example, they are not soluble in water, methanol, acetone, chloroform, or DMSO. However, they are soluble in strongly acidic aqueous solutions. It is assumed that this insolubility in normal solvents is a consequence of the material having a relatively high molecular weight (*i.e.* not a dimer or trimer species), implying that the oxidation produces a polymeric material. Further, the electrochemical and spectroscopic (see below) responses are characteristic of a conducting polymer.

The production of these polymeric films is sensitive to the ratio of the concentrations of Fe(II) and the pyridine derivative. Figure 3 shows a plot of the peak current for the catalytic oxidation at +1.5 V against the concentration ratio of [Fe(II)]/[Py]. From values of this ratio of 0.1 to 0.4, the current rises rapidly, maximizing in the range of 0.4 to 0.5. Above a ratio of 1.0, the current falls with a weaker dependence on the ratio, eventually stabilizing at a value about half of the maximum value. We have found that the best results are obtained when this ratio is in the range 0.2 - 0.5, as judged by production of thicker films that exhibit well-shaped redox responses. We have also found that other pyridine and quinoline derivatives can be oxidized in the same manner to produce films with redox responses and dependence on this ratio similar to those described here.

In addition to electrochemical investigations of these materials, we have also examined their uv-vis spectroscopy using *in situ* spectroelectrochemistry. Figure 4a shows the spectrum

of a film similar to that presented in Figure 2 above. This spectrum shows a strong uv absorbance at wavelengths in the 300-400 nm range. (Note that the ca. 300 nm cutoff of the ITO electrode leads to distortion of this peak.) This material is nearly colorless to pale yellow to the eye. Aside from this strong peak, there are no other significant peaks in the uv-vis spectrum. On reduction at -1.6 V, which is sufficiently negative to fully reduce the entire film, one observes a significant decrease in absorbance of the uv band (Figure 4b), and a corresponding increase in absorbance at wavelengths > 650 nm (Figure 4c). The color of this material is dark brown. As for the shape of the cyclic voltammogram of the film, this long wavelength band is characteristic of low bandgap conducting polymers [1]. These spectral changes are completely reversible. Figure 5 shows the dependence of the absorbance at 800 nm on potential for an experiment in which the potential was repeatedly stepped between +0.5 and -1.6 V. One sees the rapid increase in absorbance immediately after a step to -1.6 V, and the rapid decrease after a step to +0.5 V.

The voltammetry of this material as shown in Figure 2 suggests that it should exhibit significant conductivity in the approximate potential range -1.7 to +0.4, and much lower conductivity outside of this range. In order to test this notion, we have designed an experiment in which the film is probed for its ability to act as an electrode material toward a solution phase compound. Specifically, we use a compound that has two redox couples, one with a formal potential within the conductive region and one with a formal potential outside of this region. The expected response would be that the film would transfer electrons facily to and from the redox couple within its conductive range, but not for the couple outside of this range. The compound of choice for this experiment is DPPD, which has two redox couples at +0.4 V (on the edge of the conductive region) and at +0.8 V (well outside of the conductive region). Figure 6a shows the voltammetry of this compound in acetonitrile solution. Two one-electron waves of equal intensity are clearly observed at +0.4 and +0.8 V, in agreement with expectations from previous reports of the electrochemistry of this compound [48]. These correspond to the DPPD/DPPD^{•+} and DPPD^{•+}/DPPD²⁺ couples, respectively. Figure 6b shows the response for the case in which an identical DPPD concentration is used, but where the electrode is coated with a film of the conducting material. Several features of this response are worth noting. First, while both waves are seen in this case, the couple at +0.4 V is more than a factor of two more intense than that at +0.8 V. This is as expected for a film that is more conductive at +0.4 than at +0.8 V. Second, the anodic and cathodic peaks of the wave at +0.4 V have comparable currents. This suggests that the film is acting as a true electronic conductor rather than a redox mediator, because redox mediation would be more likely to exhibit chemically irreversible behavior (*i.e.* a larger peak in one direction than the other). Third, the wave at +0.4 V has the same peak separation as that at the bare electrode. This shows that the electrode kinetics for the DPPD/DPPD^{•+} couple are relatively fast on both surfaces. On the other hand, the wave for the DPPD^{•+}/DPPD²⁺ couple exhibits a slightly larger peak separation on the film-modified electrode, suggesting slightly sluggish heterogeneous electron transfer kinetics at that surface, probably due to the more insulating character of this material.

Conclusions

Taken together, the results described here show that pyridine and its derivatives can be oxidatively polymerized to produce a material that can be n-doped at very modest negative

potentials. These materials have spectral and electrochemical characteristics that are very similar to those of the conducting polymer systems that have been previously reported by Yamamoto and coworkers [16, 36-39], poly(quinolinediyl)s [40-42]. Based on the structures that they have put forth for those materials, combined with considerations of likely mechanistic pathways for production of the material described here, we present Scheme 1 as a possible structure for this material. However, a caveat to this structure is that there may be some 2-4' (*i.e.* ortho to para) coupling as well. Coupling of this type would lead to basic N sites in the material that could become protonated in acidic solutions, which would be consistent with the considerable solubility of the material in such solutions.

It is notable that the material we describe here can be n-doped at potentials as positive as 0.0 V, which makes this system one of the most easily reduced conducting polymers yet discovered. More thorough studies of the synthetic conditions and characterization of these materials are currently underway, and will be reported in a future contribution.

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Legends and Figures

Figure 1 Cyclic voltammograms of (a) lutidine (10 mM) alone, (b) iron(II) perchlorate hexahydrate (2 mM) alone, (c) potential sweep polymerization of lutidine (10 mM) with iron(II) perchlorate hexahydrate (2 mM) in the potential region from -0.8 V to 1.8 V, and (d)

the thin film obtained in c, in the potential region from -0.8 V to +0.8 V in acetonitrile solution containing 0.1 M LiClO₄. Scan rate was 50 mV/s.

Figure 2 Scan rate dependence of the cv of the obtained product on a glassy carbon electrode in acetonitrile solution containing 0.1 M LiClO₄.

Figure 3 Plot of the oxidation peak current at +1.5 V against the concentration ratio of [Fe(II)]/[Py] in acetonitrile solution containing 0.1 M LiClO₄ as a supporting electrolyte.

Figure 4 *In situ* electrochemical uv-vis spectra using ITO electrode at applied potentials of (a) +0.5 V, and (b) -1.6 V.

Figure 5 Potential dependence (reduction at -1.6 V and oxidation at +0.5 V) of absorbance at 800 nm for the obtained product on an ITO electrode in acetonitrile solution containing 0.1 M LiClO₄.

Figure 6 Cyclic voltammograms of (a) 5 mM DPPD, and (c) the thin film obtained on an ITO electrode with 5 mM DPPD in acetonitrile solution containing 0.1 M LiClO₄. Scan rate was 50 mV/s.













